Voltammetric control of thallium content in solid wastes of scintillation single crystals production

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The conditions of thallium iodide extraction by iodine-iodide solution from the wastes of coal sorbent and polishing paste (Al_2O_3 in dimethylsiloxane oligomer), its acidic decomposition by oxidizing mixtures, and the subsequent voltammetric determination studied were. Analytical procedures to determine thallium iodide as a major component in the residual product, coal sludge, and as an impurity in polishing paste wastes have been proposed. The analysis results have been shown to be free of systematic errors and as for the random ones, the relative standard deviation S_r values of 0.03 to 0.1 are typical.

Изучены условия экстракционного извлечения иодида таллия иод-иодидным раствором из отходов угольного сорбента и полировальной пасты (на основе Al_2O_3 и олигодиметилсилоксана), его кислотного разложения окисляющими смесями и последующего вольтамперометрического определения таллия. Предложены методики определения иодида таллия как основного компонента в остаточном продукте и угольном шламе и как примеси в полировальной пасте. Показано, что результаты анализа не отягощены систематическими погрешностями, а случайные погрешности характеризуются относительными стандартными отклонениями S_r, равными 0,03...0,1.

In all steps of scintillation detectors (on NaI(Tl) and/or CsI(Tl) based) production, wastes are formed and accumulated as thallium-contaminated technologic solutions, pastes, and solid materials. The wastes having high and moderate thallium iodide content are also sources of a valuable secondary raw material.

In literature, a great attention is given to the analytical control of various production wastes. However, there is no data on the wastes of scintillation alkali halide single crystals production. Independently of the thallium content of those wastes, a very high toxicity is typical feature thereof, since thallium is a highest (1st) danger class. In this connection, an analytical method providing a high determination accuracy and sensitivety is required to obtain reliable evaluation of thallium content, both as a useful major component and as a toxic impurity. Before, we have used the solubility in combination with voltammetric measurements to study the effect of sodium and cesium iodide concentrations as well as temperature on thallium iodide solubility in technologic solutions [1]. Basing on the dependences $C_{Tl} = f(T)$ and $C_{Tl} = f(C_I^-)$ (where T is temperature, °C), it has been shown that it is possible to regulate the thallium concentration in those solutions according to the destination thereof. The voltammetric data made it possible also to compare the efficiency of different methods used to remove thallium from the production solutions [2]. As to solid wastes and pastes, no similar voltammetric studies were carried out. This work is made to study the voltam-

metry potentiality in the analysis of the latter materials. Three solid waste types were taken as the study objects, namely, the residual product and coal sorbent (slime) obtained in the course of recovery pretreatment of NaI or CsI aqueous solutions by settling, filtration, and sorption, as well as the polishing paste wastes.

To evaluate the thallium content within a wide concentration range, two variants of voltammetry were applied, namely, a dropping mercury electrode (DME) in DC regime (classical polarography) and a stationary (DME) in AC regime with previous electrolytic thallium accumulation as an amalgam (stripping voltammetry). In the first case, the $Tl(I)$ reduction currents in ammonia medium were registered at the linear voltage scanning from -0.25 to -0.75 V (LP-7 polarograph); in the second one, the Tl anodic oxidation currents in ammonium acetate buffer (pH 4.8) at the voltage scanning from -0.9 to -0.2 V (a specialized polarographic unit, "Izmeritel" company, Gomel, Belarus).

Residual product analysis. The preliminary chemical composition study of the residual product (paste obtained at the technologic solution settling) have shown that, in spite of the water content varying within wide limits (from 2 to about 40 mass %), it is just thallium iodide that is the major component thereof (see Table 1). Besides, a water-soluble component (NaI or CsI) is present. So, in pastes with water content of 2 and 32 mass % (Samples 2 and 3), its concentration amounted 8 and 12 mass %, respectively, according to our estimations.

The air-dry residual product prepared to recovery contains TlI already as the major component. To determine Tl in macro-scale amounts, complexometric titration [3] is used following $Tl(I)$ oxidation to trivalent

Table 1. Thallium iodide determination results in pastes ($n = 3$; $P = 0.95$)[*]

Sample No.	1	2	3	4	5
$\overline{X}$, mass %	93	88	51	55	54
S_r	0.03	0.02	0.03	0.02	0.07

[*] Here and on: n is the number of parallel determinations; P, confidence level; S_r standard deviation for the content equal to $\overline{X}$.

state. This oxidation, however, is difficult to carry out quantitatively; moreover, accompanying metal ions hinder the titration. Although the polarography is the optimum method to determine moderate concentrations ($n \cdot 10^{-3}$ to 5 mass %), it offers substantial advantages over other methods when determining Tl as a macroscale components using small weights. This is confirmed by the metrologic characteristics obtained by us using the processing of a large data body [4].

To study, the residual product samples were taken differing considerably in the TlI level. To provide the sufficient accuracy, a special care was given to the sample pretreatment and the opening stage. To that end, a large (10 to 20 g) mass taken from a homogenized sample was dried to a constant mass and ground thoroughly in a jasper mortar. Then, at least 3 independent determinations were carried out for each sample in order to provide the sample representativity at small weights. To eliminate Tl loss at the opening stage, a collector (sodium iodide) was used. The latter was added to glasses containing the weighed samples, the samples were wetted with water and then treated successively with nitric and sulfuric acids, both concentrated. $Tl(III)$ was reduced to $Tl(I)$ using sodium sulfite.

The coincidence of TlI determination results in the initial weights (Table 2) has evi-

Table 2. Thallium iodide determination results in residual product

| Sample No.	Sample m, g $\Delta \overline{X}$ {=n}${}^{-1}_{0.95}$ BнF4	n 4	TlI mass fraction $\overline{X}$ % 4$\backslash AD3-$	S $KX3-$}$Д$	S_r KAA_3-	$\overline{X} \pm$ $-\backslash\backslash ДKA$	$\chi^2 G^*_{max,calc.}$ $3Cq$	$\chi^2 G^*_{max,tab.}$ $2\ 3w2$ $1fqA{=}3$ч№n	$F_{calc.}$ 31ч$A{-}3$	$F_{tab.}$ 1ч$A1B$
1	0.2093	7	86.43	3.8692	0.05	85±2	0.5229[*]	0.6771[*]	0.32	3.55
	0.2047	7	85.04	6.2906	0.07					
	0.2154	7	84.33	4.5974	0.06					
4	0.2102	9	54.02	1.7171	0.03	53.8±0.7	0.139	5.990	0.21	3.42
	0.1973	8	53.48	1.8775	0.04					
	0.2041	9	53.85	1.7853	0.03					

Table 3. Correctness checking of thallium iodide determination in the residual product by weight variation

Sample No.	Sample mass, g	Aliquot volume V, ml	Sample mass in aliquot m, g	n_j	TlI mass fraction $\overline{X}_j$, %	S_j^2	G^*_{max}, χ^2	$\chi^2_{tab.}$	$F_{calc.}$	$F_{tab.}$
1	0.2093	0.5	0.0010	2	86.54	6.4912	0.317	5.990	0.01	6.94
		1.0	0.0021	3	86.11	4.0737				
		2.0	0.0042	2	86.81	3.7265				
	0.2047	0.5	0.0010	2	88.16	2.3829	2.712	5.990	0.50	6.94
		1.0	0.0020	3	85.44	9.5245				
		2.0	0.0041	2	81.31	1.6122				
	0.2154	0.5	0.0011	2	86.81	3.7265	0.224	5.990	0.40	6.94
		1.0	0.0022	3	82.66	4.9793				
		2.0	0.0043	2	84.35	6.5337				
4	0.1973	0.5	0.0010	2	52.71	0.4525	5.408	5.990	2.88	5.79
		1.0	0.0039	3	52.35	0.8079				
		2.0	0.0042	3	55.13	1.3234				
	0.2041	0.5	0.0010	3	53.07	1.3234	0.5507*	0.8709*	4.09	5.14
		1.0	0.0020	3	53.01	1.5784				
		2.0	0.0041	3	55.52	0.5312				
	0.2102	0.5	0.0011	3	54.86	1.6569	0.5957*	0.8709*	0.48	5.14
		1.0	0.0021	3	53.72	1.1664				
		2.0	0.0042	3	53.48	2.4593				

denced that differences between those data are insignificant. Thus, the sample representativity at small masses can be provided.

To check the determination correctness, the weight variation method was used. From the solution of each sample, 2 or 3 aliquots of 0.5, 1.0, and 2.0 ml volume were taken, corresponding to 0.001, 0.002, and 0.004 g of the substance, respectively. The each measurement result was calculated using the addition method. The data array so obtained was processes as described in [5, 6]. The results are presented in Table 3. The homogeneity of sampling dispersions S_j^2 using the Bartlett (χ^2) or Cochrain (G^*_{max}) criteria shows that the distinctions between the dispersions are insignificant. Comparison of the mean values using the F criterion has confirmed that those differ only insignificantly at $P = 0.95$. Thus, since the found TlI mass fraction values are independent of the mass, no significant systematic error is present when it is determined in the residual product. The random error is characterized by the relative standard deviation values of 0.03 to 0.07.

The determination of Tl in polishing paste wastes and coal sorbent (slime). The squeezed paste used to polish the single

H$_3$C—Si(CH$_3$)$_2$—O—[—Si(CH$_3$)$_2$—O—]$_n$—Si(CH$_3$)$_2$—CH$_3$
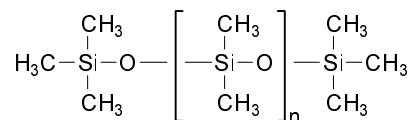
crystals contains aluminum oxide as the major component, some oligodimethylsiloxane of general formula
as well as NaI and TlI as impurities. To transform aluminum oxide into soluble state, as is known, it is to be fused with alkali fluxes at about 1000°C. This technique, however, does not provide the solubility of thallium iodide as well as does not exclude its loss as a volatile compound. When iodides were treated with concentrated nitric acid to provide acidic decomposition, a gel-like film was observed on the glass walls [7]. This observation agrees well with the data of [8] where it has been stated that when oligoorganosiloxanes are heated in the presence of an oxidant, organic groups at silicon atoms occurs oxidation

Table 4. Thallium determination results in polishing paste wastes (sample mass ratio to the iodine-iodide solution volume $m:V = 1:5$)

Sample No.	Sample mass. m, g	Tl found (mass %) at successive extractions numbered with Roman figures								Total Tl content , mass %	
		I		II		III		IV			
		x_{1i}	$\overline{x}_1$	x_{2i}	$\overline{x}_2$	x_{3i}	$\overline{x}_3$	x_{4i}	$\overline{x}_4$	$\overline{x}_{j,x}$	$\overline{x}_j$
2-03	5.1020	0.0110		0.0015		0.000041		0.000040		0.0126	
		0.0183	0.0144	0.0016	0.0015	0.000043	0.000041	0.000040	0.000040	0.0199	0.0153
		0.0139		0.0013		0.000039		0.000040		0.0152	
4-03	6.4811	0.0424		0.0024		0.000035		0.000021		0.0448	
		0.0447	0.0437	0.0022	0.0024	0.000028	0.000032	0.000014	0.000018	0.0470	0.0461
		0.0440		0.0025		0.000032		0.000018		0.0466	

along with the siloxane chains depolymerization. This results in linking of the oligomer molecules and progressive increasing of the substance viscosity up to gelatinization thereof. Thus, when decomposition techniques traditional in analytical chemistry are used, the organosilicon component is not decomposed but, in contrast, is transformed into a form that makes it impossible to determine the element to be controlled (in particular, Tl) quantitatively.

The coal slime obtained after purification of the technologic solution purification contains the coal sorbent as the major component, thallium and alkali metals iodides, as well as the industrial oil in a small amount.

When a water-soluble matrix is treated, the sample homogenization technique used for NaI(Tl) and CsI(Tl) in iodine-iodide solution [9] provides the complete dissolution of solid TlI. In the case of poorly soluble matrix having a high adsorption ability, it is not only the complete dissolution of thallium iodide but also the extraction thereof that should be provided.

The experiments carried out have shown that thallium can be extracted quantitatively out of the polishing paste and coal slime as water-soluble iodides, namely, TlI_3, TlI^-_4, or $TlI \cdot I_2$.

To that end, a mass of the polishing paste or the coal slime was placed into a conical flask, sodium iodide solution was added, the whole was heated up to $60-80°C$, acidified with concentrated nitric acid till the solution took an intense reddish-brown color, and boiled for 1 h under a cover. The cooled solution was filtered into a volumetric flask. The precipitate on filter was washed with water till the filter became colorless, and then with diluted nitric acid. The aliquots taken were subjected to acidic decomposition, similar to that used in the residual product analysis. The voltammetric measurements were carried out in ammonium solution under addition of ascorbic or acetic acid.

To study the Tl extraction completeness out of the objects mentioned, the four-time extraction was used at different ratios of the sample weight to the sodium iodide extracting solution volume (m/V). It is seen from Table 4 that the major fraction of TlI is extracted in the 1st and 2nd extraction stages, while the Tl fraction in the 3rd and 4th extractions is 0.1 to 0.5 %. It is to note that the ratio of Tl concentrations in all extracts (1st through 4th) is the same for pastes where the content thereof differs by a factor of 3. The statistic data process-

Table 5. Statistical processing of thallium determination results in polishing paste ($n = 3$, $P = 0.95$)

Exp. No.	Sample mass. m, g	m/V	Total Tl content , mass %	S	$G_{max,calc.}$	$G_{max,tab.}$	$\sigma^2_{gen.}$	$F_{calc.}$	$F_{tab.}$
1	5.1020	1:5	0.0153	0.3700	0.4684	0.7679	0.0731	2.82	4.07
2	8.8086	1:5.7	0.0222	0.3148					
3	5.2392	1:10	0.0187	0.1002					
4	5.1293	1:10	0.0180	0.2150					

Table 6. Thallium determination results in coal slime ($n = 10$, $P = 0.95$)

Decomposition technique	Tl found $\overline{X}$, mass %	S	$F_{calc.}$	$F_{tab.}$	$t_{calc.}$	$t_{tab.}$
Extractive-acidic	23.7±0.8	1.115	2.51	3.18	0.79	2.10
Acidic	24.1±0.5	0.703				

ing results presented in Table 5 using F criterion (the dispersions being homogeneous according to the Cochrain criterion) have shown that the average total (from three or four extractions) thallium contents differ insignificantly. Thus, the proposed procedure provides a complete thallium iodide extraction out of such a complex heterogeneous system as the polishing paste.

In contrast to the polishing paste, there is an alternative sample pretreatment technique for the coal slime. To that object, the direct acidic decomposition using concentrated nitric and sulfuric acids is applicable that differs only slightly from that of the residual product. This sample pretreatment technique is, however, more laborious than the extraction described above. The comparison of the thallium determination results obtained using two independent techniques to pretreatment the coal slime (Table 6) shows that already the single extraction provides the quantitative extraction of thallium, while the content thereof may be as high as 40 %.

The studies of the extractive thallium recovery out of materials to which the traditional decomposition methods are not applicable (or too complicated) by iodine-iodide solution extraction followed by voltammetric determination of thallium (Tl) both in micro- and macroscale amounts have shown that the voltammetry is suitable to control reliably and operatively any solid wastes of the alkali-halide scintillation single crystal production.

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Вольтамперометричний контроль вмісту талію у твердих відходах виробництва сцинтиляційних монокристалів

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Вивчено умови екстракційного вилучення іодиду талію іод-іодидним розчином з відходів вугільного сорбенту та полірувальної пасти (на основі Al_2O_3 та олігодиметилсилоксану), його кислотного розкладу окислювальними сумішами та наступного вольтамперометричного визначення талію. Запропоновано методики визначення іодиду талію як основного компонента у залишковому продукті і вугільному шламі та як домішки у полірувальній пасті. Показано, що результати аналізу не обтяжені систематичними похибками, а випадкові похибки характеризуються відносними стандартними відхиленнями S_r, що дорівнюють 0,03...0,1.